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Absorbent Polymers from Starch and Flour Through Graft Polymerization of Acrylonitrile and Comonomer Mixtures

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Polyacrylonitrile (PAN)-containing graft copolymers of corn starch were prepared from monomer mixtures and then saponified, and dried. Incorporation of selected comonomers lead to shorter saponification times and higher yields of adsorbent products. Substitution of flour for starch gave products which had a higher absorbency than saponified starch-g-PAN.

Absorptionspolymere aus Stärke und Mehl durch Pfropfpolymerisation von Acrylnitril- und Co-Monomergemischen. Polyacrylnitril (PAN) enthaltende Pfropf-Copolymere von Maisstärke wurden aus Monomergemischen dargestellt, verseift und getrocknet. Die Mitverwendung bestimmter Co-Monomere führte zu verkürzten Verseifungszeiten und höheren Ausbeuten an adsorbierten Produkten. Die Substitution von Stärke durch Mehl führte zu Produkten mit höherer Absorptionsfähigkeit als verseiftes Stärke-g-PAN.

1 Introduction

Graft copolymers of polyacrylonitrile (PAN) and starch, containing about equal weights of the two components, are readily prepared by allowing acrylonitrile to react with starch in an aqueous system in the presence of ceric ammonium nitrate initiator [1]. Only a small amount of ungrafted PAN is formed as a byproduct. When starch-g-PAN is treated with hot alkali, the nitrile substituents of PAN are saponified to a mixture of alkali metal carboxylate and carboxamide [2]. Isolation and drying of this saponified polymer affords a product which will absorb several hundred times its own weight of water while still remaining insoluble [3]. Films prepared by air-drying water dispersions of saponified polymer will retain their integrity when they imbibe water and will swell to form continuous sheets of gel [4]. The remarkable ability of saponified starch-g-PAN to absorb large amounts of aqueous fluids has generated considerable interest. Suggested uses for saponified starch-g-PAN range from incorporation into personal care products, such as disposable diapers, to agricultural uses, such as seed and root coating and addition to sandy soils to improve water retention.

Current research on saponified starch-g-PAN and other starch-containing absorbent polymers at the Northern Regional Research Center has as its goals the improvement of absorbent properties and salt tolerance, the simplification of

synthetic methods, and the correlation of polymer structure with absorbent properties. In this report, we will discuss the preparation of high absorbency graft copolymers by the substitution of flour for starch [5]. We also will describe the higher absorbencies and the simplified synthetic procedures which result when selected comonomers are included with acrylonitrile during graft polymerization.

2 Experimental

2.1 Materials

Globe pearl corn starch (Globe 3005) was from CPC International, and pregelatinized wheat starch was MSWS-1000 from Midwest Solvents. Yellow corn flour, bleached pregelatinized corn flour, and whole ground corn meal were from Illinois Cereal Mills. Soft wheat flour was from King Milling Company and contained 1.66% nitrogen and 0.5% ash.

Acrylonitrile, Eastman practical grade, was distilled at atmospheric pressure through a 14-in. Vigreux column, and a center cut was collected and stored at 5 °C. Reaction grade 2-acrylamido-2-methylpropanesulfonic acid (AASO₃H) was from The Lubrizol Corporation, acrylamide was Eastman reagent grade, and vinylsulfonic acid was a 40% aqueous solution from Polysciences, Inc. These three monomers were

used as received. Acrylic acid, methyl acrylate, methyl methacrylate and styrene were Eastman reagent grade and were distilled before use. Ceric ammonium nitrate was Fisher Certified ACS grade.

2.2 Graft Polymerization of Acrylonitrile and Comonomer Mixtures

A stirred slurry of 10.0 g, dry basis, of either corn starch, flour, or meal in 167 ml of water was heated for 30 min at 85–87°C while a slow stream of nitrogen was allowed to bubble through the mixture, and the mixture was then cooled back to 25°C. For experiments performed with granular starch or flour, the stirred water slurry was purged with nitrogen for 1 h at 25°C. Either 15.0 g (0.283 mole) of acrylonitrile or a mixture of acrylonitrile and a comonomer (0.283 mole total) was added to the starch or flour suspension, followed after about 1 min by a solution of 0.338 g (6.17×10^{-4} mole) of ceric ammonium nitrate in 3 ml of 1-N nitric acid. The reaction mixture was allowed to stir under nitrogen for 2 h, and in most reactions, sodium hydroxide solution was then added to give a pH of 7. The mixture was diluted with 200 ml of ethanol and the crude graft copolymer was isolated by filtration, washed with ethanol and dried *in vacuo* at 60°C. Weight percent synthetic polymer in the crude graft copolymer (% add-on) was calculated from the gain in weight due to graft polymerization.

Selected crude graft copolymers were subjected to repeated extractions at room temperature with dimethylformamide (DMF) to remove ungrafted synthetic polymer, and the weight percent of the total product which was soluble in DMF was calculated.

2.3 Saponification of PAN-Containing Graft Copolymers and Isolation of Absorbent Polymers

Dialyze and Tray Dry: A suspension of 1.00 g of crude (unextracted) graft copolymer in 20 ml of 0.5-N sodium hydroxide solution in a 125-ml Erlenmeyer flask was heated on a steam bath until the mixture assumed a red-orange color and thickened sufficiently to preclude settling on standing (about 5–15 min heating was required). The flask was loosely stoppered, to permit escape of ammonia, and was then placed in a 95–100°C oven for 2 h. The length of time in the oven needed to cause the red-orange color to fade to a light yellow (an indication that saponification had gone to completion) was noted. The reaction mixture was diluted with about 400 ml of water and dialyzed against distilled water until the pH of the dispersion was 6.4–7.2. The dispersion was then poured onto a Teflon-coated tray and dried to a thin film in a forced air oven at about 35–40°C.

Drum Dry Unpurified Product: A suspension of 4.00 g of graft copolymer in 50 ml of 0.5-N sodium hydroxide solution was heated on a steam bath for 10–15 min and was then heated in a 95–100°C oven for 3.5 h. After the reaction mixture had stood overnight at room temperature, glacial acetic acid was added to give a pH of 6.9–7.2. The reaction mass was then dried on a 7–5/8 × 6 in. diameter double-drum drier with a 0.003 in. gap separating the drums. Drums were rotated at 3 rpm and were heated with 40 psig steam.

Tray Dry Unpurified Product: A suspension of 2.00 g of graft copolymer in 25 ml of 0.5-N sodium hydroxide solution was heated on a steam bath for 10–15 min and was then heated in a 95–100°C oven for 2.5 h. The reaction mass was dispersed in 200 ml of water and glacial acetic acid was added to give a pH of 8.0–8.9. The dispersion was poured onto a Teflon-

coated tray and dried to a thin film in a forced air oven at about 35–40°C.

Methanol Precipitate: A suspension of 1.00 g of graft copolymer in 9 ml of 0.7-N sodium hydroxide solution in a 25 ml Erlenmeyer flask was heated on a steam bath for 5–10 min and was then heated in a 95–100°C oven for 3 h. The reaction mass was stirred at high speed for 1 min in a Waring Blendor with 350 ml of absolute methanol, and the precipitated solid was collected on a filter. The solid was triturated in a mortar and pestle with fresh methanol; after the resulting slurry had stood for 10 min, the solid was removed by filtration and allowed to air dry at 22°C and 50% relative humidity. Since variations in methanol content affected water absorbencies, polymers were allowed to equilibrate for at least 3 days until constant absorbency values were obtained.

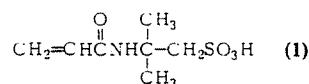
2.4 Measurement of Fluid Absorbency

To determine water absorbency of dried, saponified polymers, an accurately weighed 2–20 mg sample of polymer (amount used depended on absorbency) was allowed to soak for 30 min in 50 ml of deionized water. The swollen polymer was then separated from unabsorbed water by screening through a tared 280 mesh sieve which was 4.8 cm in diameter. The polymer on the sieve was allowed to drain for 20–30 min, and the sieve was then weighed to determine the weight of water-swollen gel. Absorbency was calculated as grams of water per gram of polymer. No correction for moisture content of the polymer (about 10–20%) was applied. Polymers with absorbencies over 1000 g/g had to be handled with extreme care to avoid break-up of the highly swollen films or particles and subsequent clogging of the sieve. A similar absorbency test was run in simulated urine (0.64 g CaCl₂, 1.14 g MgSO₄ · 7H₂O, 8.20 g NaCl, 20.0 g urea and 1000 g deionized water) with about 75 mg of polymer.

3 Results and Discussion

3.1 Use of Comonomers in Graft Polymerization

Selected comonomers were graft polymerized along with acrylonitrile onto both granular and gelatinized corn starch in the presence of ceric ammonium nitrate to give graft copolymers containing about 50–60%, by weight, of synthetic polymer. Graft polymerizations of monomer mixtures containing 1–10 mole % (3.8–30.1 weight %) of AASO₃H (see the following structural formula (1)) are shown



in Table 1 along with the times needed for alkaline saponification and the absorbencies of the products, as expressed in grams of absorbed fluid per gram of polymer. For convenience, absorbent polymers in Table 1 were isolated by dialyzing the saponification mixtures until a near neutral pH was obtained and then drying the resulting dispersions near room temperature to thin films on Teflon-coated sheets.

When any PAN-containing graft copolymer is heated in alkali, a red-orange color rapidly develops due to initial formation of highly conjugated ring structures [6]. At the end of the saponification, the red-orange color fades to a light yellow, and this color change thus serves as a good indicator of reaction completeness. Although saponifications in Table 1 were arbitrarily run for 2 h at 95–100°C, the saponification

Table 1.
Graft Copolymerization of Acrylonitrile and 2-Acrylamido-2-Methylpropanesulfonic Acid onto Corn Starch. Absorbency of Saponified Polymer.

Number	Mole % AASO ₃ H ¹⁾	Weight % AASO ₃ H	Starch granule state	Add-on ²⁾ (%)	DMF solubles ³⁾ (%)	Saponi- fication time ⁴⁾ (min)	Absorbency (g fluid per g polymer) ⁵⁾	
							H ₂ O	synthetic urine
0-Gr	0	0	Granular ⁶⁾	55	2.5	75	300	28
0-Gel	0	0	Gelat. ⁷⁾	59	12	90	1000	40
1-Gr	1	3.8	Granular	57	4.3	— ⁸⁾	380	33
1-Gel	1	3.8	Gelat.	58	8.8	65	1300	58
5-Gr	5	17.0	Granular	56	9.3	—	570	39
5-Gel	5	17.0	Gelat.	56	9.7	32	2900	62
10-Gr	10	30.1	Granular	54 ⁹⁾	16	30	970	47
10-Gel	10	30.1	Gelat.	58 ¹⁰⁾	—	28	5300	73

1) AASO₃H = 2-acrylamido-2-methylpropanesulfonic acid.

2) Weight % synthetic polymer in the dry reaction product.

3) Weight % of the dry reaction product dissolved by exhaustive extraction with dimethylformamide (DMF).

4) As indicated by the color change from red-orange to yellow. All saponifications were run for 2 h.

5) Isolated by dialysis and tray drying.

6) Starch-water slurry maintained at room temperature.

7) Starch-water slurry heated for 30 min at 85–87°C and then cooled to room temperature before graft polymerization.

8) Not determined.

9) Graft copolymer contains 0.71% sulfur.

10) Graft copolymer contains 1.29% sulfur.

times given in the tables are the times required for loss of the red-orange color.

Extraction of homopolymers from crude graft copolymers with DMF at room temperature removed, in most instances, less than 10% of each product as DMF solubles; moreover, these soluble fractions were not all homopolymer, as evidenced by carbohydrate absorptions in infrared spectra. Grafting efficiencies were therefore high in these polymerizations. Since each reaction mixture was neutralized to pH 7 before product isolation, poly(AASO₃H) in the copolymer is largely in the DMF-insoluble sodium salt form, poly(AASO₃Na), rather than as the free sulfonic acid. However, due to the solubility of PAN in DMF, we would expect that poly(acrylonitrile-co-AASO₃Na) would also be DMF-soluble at low concentrations of AASO₃Na. Alkaline saponifications were run on unextracted polymers.

Two important conclusions may be drawn from Table 1. First, the incorporation of AASO₃H as a comonomer along with acrylonitrile gives graft copolymers which require significantly shorter saponification times. Shortening of reaction time is, of course, of critical importance if the absorbent polymer is to be produced economically on a large scale. Second, use of AASO₃H in conjunction with acrylonitrile gives saponified graft copolymers from both granular and gelatinized starch which absorb larger amounts of aqueous fluids than their counterparts prepared from acrylonitrile alone. Use of gelatinized starch with a monomer mixture containing 10 mole % AASO₃H results in a saponified polymer which will absorb over 5000 times its weight of deionized water. Granular starch with the same monomer mixture affords a saponified polymer which absorbs about as much water as saponified starch-g-PAN prepared from gelatinized starch but in the absence of comonomer. It is highly significant that polymers with absorbencies of almost 1000 g/g can be prepared without the need for starch gelatinization by simply including AASO₃H in the polymerization recipe. Graft polymerization onto granular starch not only shortens processing time and saves energy which would be used to perform the gelatinization step, but

also yields a granular graft copolymer which may be easily isolated from a reaction mixture by filtration or centrifugation, purified by water washing, and stored if necessary before alkaline saponification.

Since dialysis followed by tray drying would not be an acceptable isolation method for large-scale production of absorbent polymers, we examined some more practical methods for product isolation and determined how these methods effected water absorbency (Table 2). When crude saponification mixtures were drum-dried, with no further treatment other than to adjust the pH to near neutrality with glacial acetic acid, products had greatly reduced absorbencies, as compared with values in Table 1, and absorbency differences between individual products were not as large. In fact, when gelatinized starch was used, absorbencies were about the same regardless of the AASO₃H content of the monomer mixture. With granular starch, significant increases in absorbency were realized with monomer mixtures containing 5 and 10 mole % AASO₃H.

Table 2.
Water Absorbencies of Saponified Polymers from Table 1. Dependence on Isolation Method.

Number ¹⁾	Absorbency (g H ₂ O per g polymer)		
	Drum dried unpurified product	Tray dried unpurified product	Precipitate with methanol
0-Gr	180	—	230
0-Gel	320	430	1500
1-Gr	240	—	260
1-Gel	330	980	2600
5-Gr	320	—	590
5-Gel	290	1800	1800
10-Gr	350	—	1000
10-Gel	310	1600	2500

1) From Table 1.

A second method which we used to isolate absorbent polymers was to dilute the crude saponification mixtures with water, adjust the pH to near neutrality with acetic acid, and dry the resulting dispersions to thin films near room temperature on Teflon-coated sheets. If various substrates, e. g., cellulose fibers, paper, or clay, were to be coated with a small percentage of absorbent polymer to increase their absorbency, a drying method similar to this would probably be used. Although granular starch-based polymers were not isolated by this procedure, those derived from gelatinized starch showed large increases in absorbency when prepared with AASO₃H, even though the absorbency of the 10 mole % AASO₃H product was lower than expected, based on Table 1. Since drying conditions used for these absorbent polymers were similar to those used for the dialyzed polymers of Table 1, differences in these two sets of absorbency data show the detrimental effects of inorganic salts on absorbency. The data also suggest that the low absorbencies of drum dried products are due to excessive heat during drying, since these and the drum-dried polymers have similar inorganic salt contents.

Finally, absorbent polymers were isolated by precipitation with methanol followed by air drying. Polymers prepared from gelatinized starch with 0 and 1 mole % AASO₃H showed higher water absorbencies after methanol precipitation than they did after dialysis and tray drying, while those prepared with larger amounts of AASO₃H showed higher absorbencies with the dialysis and tray-drying technique. Examination of granular starch-based products showed only minor differences in absorbency between the dialyzed and tray-dried samples of Table 1 and the methanol precipitated products of Table 2. If we consider the four methanol precipitated products from granular starch, it is obvious that incorporating AASO₃H in graft polymerization mixtures leads to significantly higher water absorbencies. The beneficial effect of AASO₃H on the absorbency of methanol precipitated polymers is less, however, when gelatinized starch is used.

Sulfur analyses were run on the granular and gelatinized starch graft copolymers prepared with 10 mole % AASO₃H, and these analyses showed that synthetic moieties contained only 2.3 and 4.2 mole % AASO₃H, respectively. Analyses of saponified graft copolymers, however, showed that 80–85% of these AASO₃H repeating units were still present in the polymer and had not suffered alkaline saponification.

Although reaction mixtures were normally neutralized with sodium hydroxide before product isolation, we also ran a few graft polymerizations with AASO₃H as a comonomer without neutralizing the acidic reaction mass before isolating and drying the product at 60°C. However, these graft copolymers gave saponified polymer films, after dialysis and tray drying, which in many instances were inferior as absorbents for deionized water, since they swelled to such a large degree that they lost their film integrity. It was thus logical to assume that the sulfonic acid groups in the synthetic polymer were causing hydrolysis of the starch moiety under the conditions of drying. Although these saponified graft copolymer films swelled excessively in water, many of them maintained their integrity and had good absorbent properties when placed in electrolyte solutions. For example, a saponified graft copolymer with 56% add-on prepared from a monomer mixture containing 5 mole % AASO₃H and 95 mole % acrylonitrile absorbed 87 g of synthetic urine per gram of polymer.

If the percentage of AASO₃H in the monomer mixture was sufficiently high, the resulting graft copolymers showed a high enough affinity for water to function as absorbents for

aqueous fluids without saponification, even though the free sulfonic acid groups made the polymer-water system strongly acidic. For example, a graft copolymer with about 54% add-on prepared from a mixture of 31 mole % (63.6 weight %) AASO₃H and 69 mole % acrylonitrile absorbed 580 times its weight of deionized water and 21 times its weight of synthetic urine. The pH of a viscous 0.67% dispersion of this polymer in water was 2.5. The ability of a graft copolymer of this type to swell and absorb water under highly acidic conditions is an extremely useful property not found in any of the saponified starch-g-PAN graft copolymers previously prepared. Indeed, when the sodium carboxylate groups of saponified starch-g-PAN are converted to the carboxylic acid form (usually at a pH of about 3), the polymer precipitates from dispersion as a rubbery mass, which shows a greatly reduced absorptive capacity for aqueous fluids [2].

Graft polymerizations of mixtures of acrylamide (10 or 20 mole %) and acrylonitrile onto both granular and gelatinized corn starch and the saponification of the resulting graft copolymers are shown in Table 3. Extraction with DMF removed only minor amounts of soluble polymer, and saponifications were run on the unextracted products. Although the absorbencies of tray dried films cast from the saponified graft copolymers after dialysis were in most cases the same or somewhat less than those of the corresponding products prepared in the absence of comonomer, the times needed for alkaline saponification were shortened considerably when acrylamide was included in polymerization mixtures. For example, a graft copolymer prepared from a mixture of 20 mole % acrylamide and 80 mole % acrylonitrile was completely saponified in a remarkable 12–13 min. Since all saponifications were arbitrarily run for 2 h, regardless of the time of the observed color change, the last saponification in Table 3 was rerun and the saponification mixture removed from the oven and worked up after 13 min to see if the shortened saponification time would adversely effect absorbency. The saponified polymer film absorbed 720 g of water per gram of polymer, in reasonable agreement with the value of 660 in Table 3.

Table 3.
Graft Copolymerization of Acrylonitrile and Acrylamide onto Corn Starch. Absorbency of Saponified Polymer.

Mole % AA ¹⁾	Weight % AA	Starch granule state	Add-on (%)	DMF solubles (%)	Saponi- fication time (min)	Absorbency (g fluid per g polymer) ²⁾	
						H ₂ O	Synthetic urine
0	0	Granular	55	2.5	75	300	28
0	0	Gelat.	59	12	90	1000	40
10	12.9	Granular	58	4.8	—	460	34
10	12.9	Gelat.	60	7.2	27	880	43
20	25	Granular	58	4.3	12	300	30
20	25	Gelat.	60	5.2	13	660	28

1) AA = acrylamide.

2) Isolated by dialysis and tray drying.

Five other monomers were copolymerized with acrylonitrile onto gelatinized corn starch to determine their effect on saponification time and on the absorbency of saponified graft copolymer films isolated by dialysis and tray drying (Table 4). Acrylic acid increased water absorbency of the saponified graft copolymers and shortened the time needed for saponification. A shortened saponification time was also obtained with 10 mole % methyl acrylate. Although inclusion

Table 4.
Graft Copolymerization of Acrylonitrile and Selected Comonomers onto Gelatinized Corn Starch. Absorbency of Saponified Polymer.

Comonomer	Mole % comonomer	Weight % comonomer	Add-on (%)	Saponi- fication time (min)	Absorbency (g fluid per g polymer) ¹⁾	
					H ₂ O	Synthetic urine
None	0	0	59	90	1000	40
Vinylsulfonic acid	5	9.7	56	105	1200	49
Acrylic acid ²⁾	5	6.6	49	30	1500	42
Acrylic acid ³⁾	10	13.1	48	20	1600	47
Methyl acrylate	10	15.2	61	40	1000	38
Methyl methacrylate	10	17.3	60	95	440	26
Styrene	10	17.8	55	70	230	21

1) Isolated by dialysis and tray drying.

2) Twice the usual amount of ceric ammonium nitrate was required to initiate polymerization.

3) Four times the usual amount of ceric ammonium nitrate was required to initiate polymerization.

of vinylsulfonic acid also gave a saponified polymer with higher absorbency, the saponification time was somewhat longer. This was a surprising result, since one might expect behavior analogous to AASO₃H. When 10 mole% of either methyl methacrylate or styrene was included with acrylonitrile in the graft polymerization, absorbency values of the saponified products were lower than those of saponified starch-g-PAN, and there was little or no reduction in saponification time.

3.2 Graft Polymerization of Acrylonitrile onto Flour and Meal

Acrylonitrile was graft polymerized onto a series of flour and meal samples, which had either been slurried in water at room temperature or heated in water at 85 °C to gelatinize the starch component (Table 5). Comonomers were not used. With the exception of the reaction with whole ground corn meal, which used twice the normal amount of ceric ammonium nitrate initiator, graft polymerizations were carried out in a manner identical to that normally used with starch and gave products with comparable values for % add-on.

A major difference between these reactions and previous polymerizations onto corn starch was the relatively high percentage of polymer which was dissolved on extraction with DMF. Infrared spectra of these soluble fractions showed

them to be largely ungrafted PAN, with the exception of the fraction from the bleached pregelatinized corn flour product, which contained considerable carbohydrate. Since ungrafted PAN would not be removed from the graft copolymer before saponification in any practical process, the entire reaction product from graft polymerization was saponified to obtain the absorbent polymer.

Although it is apparent from Table 5 that saponification times have not been significantly shortened by substituting flour or corn meal for starch, the fluid absorbencies of saponified polymers isolated by dialysis and tray drying have been markedly increased by this substitution. Of particular interest is the absorbent polymer prepared from ungelatinized yellow corn flour, which had an absorbency almost equal to an analogous product prepared from gelatinized corn starch. Not only is flour often a cheaper raw material than starch, but omission of the gelatinization step would result in a significant cost savings in any commercial process.

As with the AASO₃H-containing polymers, we investigated some practical methods for the isolation of the absorbent polymers prepared from granular and gelatinized yellow corn flour and determined the effects of these isolation methods on water absorbency (Table 6). As observed in Table 2, drum drying of crude reaction mixtures produced polymers having relatively low absorbencies; only minor differences were found between flour-based polymers and starch-based polymers. When the unpurified reaction mixtures derived

Table 5.
Graft Polymerization of Acrylonitrile onto Flour and Meal. Absorbency of Saponified Polymer

Number	Substrate	Pretreatment of substrate slurry (°C)	Add-on (%)	DMF solubles (%)	Saponi- fication time (min)	Absorbency (g fluid per g polymer) ¹⁾	
						H ₂ O	Synthetic urine
CF-Gel	Yellow corn flour	85	53	26	105	2600	57
CF-Gr	Yellow corn flour	25	40	22	> 60	900	32
PCF	Bleached pregelat. corn flour	25	58	27	> 60	2700	76
CM-Gel	Whole ground corn meal ²⁾	85	42	—	75	1900	39
WF-Gel	Soft wheat flour	85	52	34	> 85	2100	44

1) Isolated by dialysis and tray drying.

2) Twice the normal amount of ceric ammonium nitrate was required to initiate polymerization.

Table 6.
Water Absorbencies of Flour-Based Polymers vs Starch-Based Polymers. Dependence on Isolation Method.

Number	Absorbency (g H ₂ O per g polymer)		
	Drum dried unpurified product	Tray dried unpurified product	Precipitate with methanol
0-Gr ¹⁾	180	—	230
0-Gel ¹⁾	320	430	1500
CF-Gr ²⁾	200	—	500
CF-Gel ²⁾	270	690	1200

1) From Table 2.

2) From Table 5.

from gelatinized flour and starch were tray dried, the use of flour in the graft polymerization resulted in a significant increase in absorbency. When absorbent polymers were isolated by methanol precipitation, the gelatinized flour-based polymer exhibited a lower water absorbency than its starch counterpart, in contrast to the results in Table 5 for dialyzed and tray dried films. The methanol precipitated absorbent from granular flour, however, showed a significantly higher absorbency than that prepared from granular starch.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Summary

Polyacrylonitrile (PAN)-containing graft copolymers of corn starch were prepared from monomer mixtures obtained when

selected comonomers were substituted for a portion of the acrylonitrile. Graft copolymers were then saponified and the saponified polymers dried to form absorbents for aqueous fluids. Use of 2-acrylamido-2-methylpropanesulfonic acid as a comonomer resulted in shorter saponification times and more absorbent products. Incorporation of acrylamide into the polymerization mixture similarly shortened the time needed for saponification. Vinylsulfonic acid, acrylic acid, methyl acrylate, methyl methacrylate and styrene were also used as comonomers, and their effect on saponification time and on absorbency of the saponified polymer was examined. Substitution of flour or corn meal for starch in the ceric initiated graft polymerization of acrylonitrile gave polymers which, after saponification, had a higher absorbency for aqueous fluids than saponified starch-g-PAN.

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